Piezoresistive Nanocantilevers for Magnetic Resonance Force Microscopy(力検出型磁気共鳴顕微鏡のためのピエゾ抵抗型ナノカンチレバー)

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論文内容要旨

The invention of the scanning tunneling microscope (STM) and the atomic force microscope (AFM) in the 1980s opened a new era of nanotechnology and nanoscience. By combining scanning probe microscopy with magnetic resonance imaging, the magnetic resonance force microscopy (MRFM) was proposed by J. A. Sidles in 1992. MRFM is based on mechanical measurement of attonewton-scale magnetic forces between nuclear spins in a sample and a nearby magnetic tip. It has succeeded in detecting a single electron spin. Two-dimensional imaging of nuclear spins has been extended to a spatial resolution of better than 100 nm. Despite the many challenges, there is strong motivation to extend MRFM to finer resolution, especially if the nanometer scale can be reached. At the nanometer scale, one might hope to directly and nondestructively image the 3D structure of individual macromolecules and molecular complexes. Such a powerful molecular imaging capability could be of particular interest to structural biologists trying to unravel the structure and interactions of proteins. The key to pushing magnetic resonance imaging to the nanoscale is detection sensitivity of the MRFM system, which is directly correlated to magnetic field gradient and the force sensitivity of the cantilever.

Nanocantilevers exhibit higher sensitivity and lower air damping effect than that of microcantilevers either by theoretical analysis or experiments. However, the approaches to displacement transduction for microcantilevers such as capacitive detection and optical readout are not applicable to nanocantilevers. The signal in capacitive detection for nanocantilevers is typically overwhelmed by uncontrollable parasitic effects. Optical detection is not applicable when the device dimensions are far below the wavelength of the illumination used due to the diffraction effect. Piezoresistive displacement transduction is most used for self-sensing nanocantilevers. It is reported that an unprecedented mass resolution less than 1 attogram in air at room temperature has been achieved with a nanocantilvers based on piezoresistive thin metal film. The high resonance frequency and force sensitivity of the piezoresistive cantilevers make it possible to be utilized as an MRFM probe for living cell imaging application. Furthermore, it was found that the longitudinal piezoresistance coefficient of silicon increases by decreasing the cross-section area and the transverse piezoresistance coefficient decreases by increasing the aspect ratio of the cross-section. A giant piezoresistance has been investigated in silicon nanowires. In addition to the scaling effect based on mechanical analysis, this giant piezoresistance effect also contributes to the sensitivity improvement of nanocantilevers. This thesis describes the modelling, fabrication, and characterization of the piezoresistive nanocantilevers for the MRFM application. The schematic structure of the piezoresistive nanocantilevers is shown in Fig. 1.

For cantilever-based force sensors, the operation schemes include the static mode, AM mode and FM mode. The FM mode has been widely used in AFM and MRFM experiments due to its high sensitivity and detection speed. However, all the reported design methods for piezoresistive cantilever were based on the assumption that cantilevers operated at static mode. After calculating the force resolution required in MRFM experiments to realize high resolution at room temperature and cryogenic temperatures, we introduced a design model for a piezoresistive cantilever which is operated in the FM mode. The sensitivity and noise were modeled using the parameters which include the spring constant, resonant frequency, piezoresistive displacement sensitivity, and resistance of the piezoresistor. The noise including the thermomechanical noise of the cantilever, the Johnson noise and the flicker noise of the piezoresistor was analyzed by converting it into a frequency variation which limits the minimum detectable force of the cantilever. We described methods of determining the spring constant and resonant frequency for cantilevers with arbitrary geometries using their geometrical and material parameters. By introducing an efficiency factor with consideration of the doping profile in the cantilever's thickness direction, the displacement sensitivity of the piezoresistive nanocantilevers were calculated. We also calculated the resistance of the piezoresistor using an effective resistivity parameter by considering the carrier mobility variation with the impurity concentration. Using the above modeling results, we were able to build a design model for piezoresistive nanocantilevers based on their geometrical parameters. This model was used to simulate the minimum detectable force variation with various parameters of the cantilever. We found that the minimum detectable force is ultimately limited by the Johnson noise of the piezoresistor and it can be reduced by increasing the cantilever length and decreasing the supporting leg length and width. An optimized nanocantilever was calculated to be able to achieve a force resolution of 220 $aN/Hz^{1/2}$ at room temperature and 0.1 $aN/Hz^{1/2}$ at a temperature of 0.1 K, which would greatly improve the spatial resolution of the MRFM experiments.

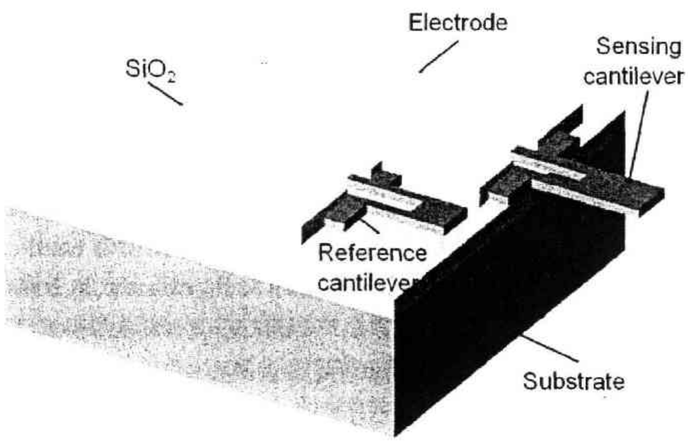
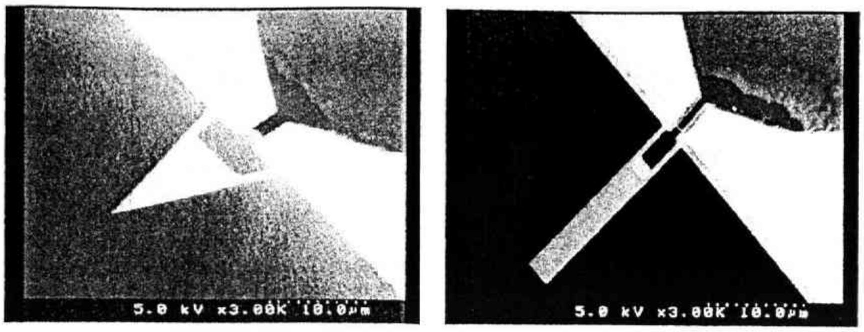


Fig. 1 Schematic structure of the piezoresistive nanocantilevers

For the fabrication of the piezoresistive nanocantilevers, the starting material is a high-resistivity silicon-on-insulator (SOI) wafer. The active layer is (100)-oriented single crystal silicon with a thickness of 100 nm. The thickness of the buried oxide (BOX) layer and handling layer are 200 nm and 300 mm, respectively. In order to confine the boron diffusion in the top half of the active layer, spin-on diffusion and rapid thermal annealing (RTA) process are utilized. Boron dopant (B153 from Filmtronics Inc.) is used for diffusion. In order to optimize the doping condition, characterization experiments are done with different RTA conditions. After RTA, hydrofluoric acid (HF) solution is used to remove the dopant glass on the surface of the wafer. The doping profiles are measured using second ion mass spectroscopy (SIMS). The SIMS analysis results of the boron diffusion at 1173 K with different RTA times. Doped layers as thin as 40 nm can be achieved for both boron and phosphor diffusion. Electron beam (EB) lithography with a positive resist ZEP520A is used to form the pattern of electrodes and alignment masks. After deposition of a 60-nm-thick gold film with 20-nm-thick chromium as an adhesive layer using sputtering, the electrodes and alignment masks are formed by lift-off process. EB lithography is utilized to form the pattern of the nanocantilevers, which are aligned to the electrodes with a resolution better than 50 nm. The active layer is etched by fast atom beam (FAB) to pattern the nanocantilevers, and the EB resist is removed by O_2 plasma asher. The pattern of electrode pads is formed by photolithography, plasma sputtering of gold film, and lift-off process. The backside of the substrate is patterned by photolithography and etched by a deep reactive ion etching (DRIE). Photoresist is patterned to protect the cantilevers and electrodes on the top side in the following processes for releasing the nanocantilevers. After removing the SiO_2 by buffered hydrofluoric acid (BHF), XeF_2 gas phase etching is utilized from the front side to precisely control the released length of the cantilevers. BHF is employed again to remove the BOX layer behind the cantilevers. Finally, the photoresist is removed by N-Methyl-2-pyrrolidinone and critical point drying is done to avoid the stiction. Due to the high uniformity and controllability of XeF2 vapor-phase etching, over-etching problem in cantilever release is suppressed. The scanning electron microscope graphs of fabricated piezoresistive nanocantilevers are illustrated in Fig. 2.



(a) (b)

Fig. 2 SEM micrograph of fabricated piezoresistive nanocantilevers.

The displacement sensitivity of the nanocantilevers was evaluated by measuring the resonance response using optical read-out and piezoresistive detection method, respectively. The nanocantilevers were actuated by a piezoelectric actuator and the vibration was both optically and piezoresistively detected. Before the piezoresistive detection, the current-voltage (I-V) characteristic of the nanocantilever was measured. A piezoresistive signal downmixing method was utilized in our measurement. In this method, ac biasing voltages with 180° phase shift are applied oppositely to the nanocantilever and the reference resistor, to null the bias voltage at the bridge point. The nanocantilever is actuated by a piezoelectric actuator at a frequency offset from ac biasing voltage by a mount of Δf. The output signal at the bridge point contains frequency component of Δf, which is downmixed by the piezoresistor. A displacement sensitivity as high as 26 ppm/nm was achieved for a nanocantilever with a length of 19 μm, a leg width of 1.0 μm, leg length of 4.0 μm, thickness of 100 nm.

A softening spring nonlinear effect was detected for many nanocantilevers with "soft" support due to the over-etching in cantilever release process. The nonlinearity of the nanocantilevers was modeled based on the equation of motion for forced cantilevers with viscous damping. By fitting the resonance response of the nanocantilevers using this model, the nonlinearity parameter was deduced. It was found that the nonlinearity parameter rises with increasing the cantilever length if other dimensions remain constant. It was experimentally demonstrated that the dimensions of the "soft" supporting plates and the surface pre-stressed conditions of the cantilevers play an important role in the cantilever's nonlinear behavior.

In order to evaluate the applicability of the piezoresistive nanocantilevers at low temperatures, we investigated the temperature dependence of the mechanical and electrical properties of boron doped piezoresistive nanocantilevers. For a piezoresistive nanocantilever with a length of 20 μm and a width of 4 μm as shown in Fig. 2(b), the resonance responses are measured as shown in Fig. 3. By measuring the resonance response of the nanocantilever ranging from room temperature to 78 K, we identified that the frequency increases with reduction of the temperature by a temperature coefficient of 210 ppm/K. The influence of the elastic stress due to boron doping is a possible source for the ultra-high temperature coefficient of the resonant frequency. The Q factor increases up to 3.5 times of the room temperature value while the temperature decreasing down to 78 K. It probably originates from the surface defects related intrinsic dissipation mechanism. The experiment shows the existence of a peak valve of longitudinal piezoresistance coefficient in the range of 80 - 90 K for the nanocantilevers in our experiments. Further theoretical and experimental investigations are required to understand this phenomenon. The temperature dependence of the electrical resistances of the piezoresistive nanocantilever was measured. From 300 K to 40 K, the resistance remains constant, while the resistance abruptly increases up to 1 MΩ at 40 K. Then the resistance keeps constant again and abruptly increases up to 7 MΩ at 20 K. The reference piezoresistor shows a similar characteristic. This "quantum" metal-insulator transition at a temperature as high as 40 K was observed for the first time. Metal-insulator transition refers to changes in the transport properties of a given material at low temperatures. Transport properties are determined by the disorder due to presence of impurities, and various interactions effects such as Coulomb interactions. The high transition temperature is probably due to the high impurity density and strong disorder property of our devices. The "quantum" metal-insulator transition might be the first experimental demonstration of the discontinuous transition behavior suggested by Mott. This phenomenon is related to the shallow doping profile and fine cantilever legs. As the piezoresistive nanocantilevers are expected to be used in high magnetic field environment, we investigated the electrical resistance variation with the magnetic field strength. The

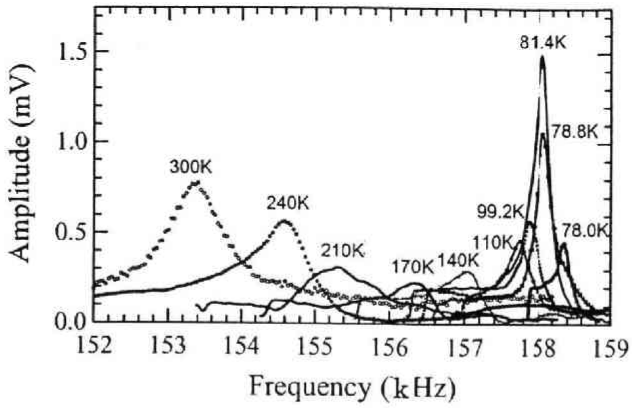


Fig. 3 Temperature dependence of the resonance response of the piezoresistive nanocantielver shown in Fig. 2(a).

electrical resistance of the nanocantilever increases by applying a magnetic field which is parallel with the cantilever's longitudinal direction at 10 K. The high magnetic field aligns the holes and suppresses hole-hole interaction. As a result, the delocalizing effect of the hole-hole interaction is quenched by the external magnetic field, and the electrical resistance rises as the magnetic field is increased. Though the positive magnetoresistance effect will slightly increase the thermoelectrical noise in sensing experiments, it just decreases the force resolution of the nanocantilever at a very small amount and doesn't affect the nanocantilevers for the MRFM application.

We introduced two kinds of schemes to develop piezoresistive nanocantilevers with a magnet tip. One method is to mount a micromagnet on the apex of the nanocantilever by a micropositioner and fix the micromagnet permanently on the cantilever by an electron beam carbon deposition method in a conventional scanning electron microscope system. However, this method cannot precisely control the geometry of the micromagnet. As a result, it is very difficult to achieve a high magnetic field gradient using this method. The other method is to fabricate the nanocantilevers with integrated nanomagnets using the micromachining technique. Using the EB lithography and lift-off processes, we succeeded in aligning the nanocantilever to nanomagnets and electrodes with an nanoscale precision. A MRFM experiment setup using nanocantilevers was built to demonstrate the applicability of piezoresistive nanocantilevers for the MRFM application. In the experiment setup, the DPPH samples were mounted on the tip of the cantilever, and the magnetic field and the field gradient were generated by a permalloy wire with a diameter of 0.7 mm. An additional coil was concentrically mounted around the permalloy wire to modulate the magnetization at the same frequency with the cantilever. The RF excitation coil were tuned and matched to 1.32 GHz with an impedance near 50 Ω to reduce the power loss.

In summary, we proposed a design model for piezoresistive nanocantilevers used in the frequency modulation mode. The piezoresistive nanocantilevers were fabricated using nanomachining techniques such as electron beam lithography, fast atom beam etching, etc. The piezoresistive nanocantilever demonstrates a very high displacement sensitivity and force resolution. The temperature dependence of the mechanical and electrical properties of the nanocantilevers was characterized. In order to demonstrate the applicability of the piezoresistive nanocantilever for the MRFM application, we fabricated piezoresistive nanocantilevers with integrated nanomagnets and constructed an experiment setup for the MRFM experiments.

論文審査結果の要旨

半導体微細加工技術を発展させたマイクロ加工技術を用いると，さまざまな機能を集積化した小型のデバイスが実現できる。一方，振動型の力センサは小型化すると高感度化し，熱機械ノイズの影響を低減できる。マイクロ加工技術を用いた振動型の力センサを小型化すると，アトニュートンのオーダーの非常に小さな力が検出でき，さまざまな応用が拓かれる。この力センサに磁性体をのせると高感度な磁気センサになり，磁気スピンの変化などが検出できるため，磁気共鳴と組み合わせて細胞などの微小な試料の3次元のイメージングができることが提案されている。本論文は，微弱な磁気共鳴を検出しナノスケールでの物質の3次元構造を測定するためのマイクロマシンプローブに関する研究をまとめたもので，全編7章からなる。

第1章は序論であり，研究背景や目的について述べている。

第2章では，磁気共鳴や変位検出方法，ピエゾ抵抗について述べている。磁気共鳴型のセンサの各種方式について論じ，ピエゾ抵抗検出型の力検出型磁気共鳴力顕微鏡用のプローブを提案している。これは，高分解能なイメージングを実現するために重要な成果である。

第3章では，高感度に力を測定するための力センサに関する設計論について述べ，ピエゾ抵抗型センサの感度やノイズ，形状に依存する因子，磁石効果などのサイズ効果について論じている。これは，センサを高感度化し，熱機械ノイズの影響をできるだけ低減するために重要な知見である。

第4章では，半導体の微細加工技術を利用した，ピエゾ抵抗型のナノスケールのプローブの作製方法についてまとめている。力センサとして高感度するために，シリコンを100nm程度まで薄くし，その表面に薄くピエゾ抵抗型の歪センサを作製する手法について述べている。これは，高感度な力センサの変位検出法として重要な成果である。

第5章では，作製したピエゾ抵抗型力センサを評価した結果についてまとめている。小型化した力センサが強い機械的な非線形性を示すことを実験的に見出しており，センサの形状が非線形性にあたえる影響について評価している。これは，センサのダイナミックレンジを決める大きな要因であり，重要な知見である。ピエゾ抵抗型センサ　の低温での特性について評価し，低温では機械損失が低減しQ値が大きくなること，およびピエゾセンサのゲージファクターが増加し感度が向上することを見出している。これは，ピエゾ抵抗型力センサが有効であることを示す非常に重要な成果である。

第6章では，磁気共鳴のイメージングをするための装置の作製や，磁石を取り付けたプローブの作製方法についてまとめてある。これは，ピエゾ抵抗型のセンサを磁気イメージングするために必要不可欠であり，有益な成果である。

第7章は，結論であり，各章の成果をまとめている。

以上要するに本論文は，ピエゾ抵抗型の変位センサを内蔵したナノスケールの力検出型磁気共鳴プローブを開発し，低温での電気機械特性により微弱な力センサとして有効であることを示し，力検出型磁気共鳴イメージングに利用できることを示したものであり，ナノメカニクスおよび機械工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。